

Rapid communication

Photoluminescence properties of a novel phosphor, $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{RE}^{3+}$ ($\text{RE} = \text{Eu}, \text{Tb}$)

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Abstract

The new oxyborate phosphors, $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{Eu}^{3+}$ (NLBO:Eu) and $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{Tb}^{3+}$ (NLBO:Tb) were prepared by solid-state reactions. The photoluminescence characteristics under UV excitation were investigated. The dominated emission of Eu^{3+} corresponding to the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ is located at 613 nm and bright green luminescence of NLBO:Tb attributed to the transition ${}^5D_4 \rightarrow {}^7F_5$ is centered at 544 nm. The concentration dependence of the emission intensity showed that the optimum doping concentration of Eu and Tb is 30% and 10%, respectively.

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1. Introduction

Rare-earth-activated phosphors have attracted much attention for their well-defined transitions within the 4f shell [1]. Eu^{3+} is an excellent activator for the red-emitting phosphor, and Tb^{3+} for the green-emitting. Eu^{3+} - or Tb^{3+} -doped borate phosphors have been extensively studied in the past decades. The borates are good candidates as the host lattices for luminescence because of their large band gap [2–6]. For example $(\text{Y}, \text{Gd})\text{BO}_3:\text{Eu}$ is widely used in plasma display panel applications [7–9]. And $\text{YBO}_3:\text{Tb}^{3+}$ prepared by hydrothermal synthesis is a promising phosphor for plasma display panels and hydrargyrum-free lamps [10,11]. SrBPO_5 -related phosphors ($\text{SrBPO}_5:\text{Tb}^{3+}, \text{Ce}^{3+}$ and Na^+) exhibit enhanced luminescence and can be utilized as green phosphors in tricolor lamps [12].

In 2001, a new sodium lanthanum oxyborate, $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8$ (NLBO), was obtained by Wu et al. [13]. Gravereau et al. [14] reported the preparation of the single crystal and solved its crystal structure. It belongs to the hexagonal system with space group $P-62m$. Its basic

structure is composed of BO_3 planar triangle, LaO_9 polyhedra, LaO_8 polyhedra, and NaO_6 polyhedra. The first nearest La–La distance and the second nearest La–La distance in the structure is 3.691 and 4.030 Å, respectively [15]. Generally, a weak crystal field may be expected at the rare-earth sites due to the high degree of covalency in the BO_3 anions, while larger interatomic distance reduces exchange coupling and multipolar interactions. These are in agreement with a requirement for weak concentration quenching [16]. It is worthwhile therefore to study the luminescence properties of active rare-earth ions in new oxy borate $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8$. To our knowledge, photoluminescence (PL) properties of NLBO: RE^{3+} ($\text{RE} = \text{Eu}, \text{Tb}$) under ultraviolet (UV) excitation have not been reported. In this paper, we report the preparation of NLBO: RE^{3+} ($\text{RE} = \text{Eu}, \text{Tb}$) and their luminescent characteristics in UV region.

2. Experiment

Eu^{3+} -doped NLBO was synthesized by solid-state reactions. The stoichiometric amount of starting materials Na_2CO_3 (A.R.), H_3BO_3 (A. R.), La_2O_3 (99.99%) and Eu_2O_3 (99.99%) were mixed in an agate mortar, except

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common La corner. In the structure, La^{3+} ion has two types of coordinations: La1O_8 (La1 in 3g) and La2O_9 (La2 in 6i) [14,20]. The symmetry of La^{3+} is C_{2v} and C_s , respectively (Fig. 3). Because the crystal structure offers two different sites for lanthanum, Eu^{3+} may replace either La1 with the symmetry of C_{2v} , or else La2 with the symmetry of C_s .

The electrical dipole transition ${}^5D_0 \rightarrow {}^7F_2$ is hypersensitive to the local environment, while the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$ is not affected much by the ligand field around the Eu^{3+} . Therefore the ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratio (R/O value) is a measure of the rare-earth ion site symmetry. A lower symmetry of the crystal field around Eu^{3+} will result in a higher R/O value [21]. When the intensities of ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ are comparable, the features imply a higher site-symmetry of Eu^{3+} [22]. For NLBO:Eu^{3+} the ${}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratio (R/O value) is 1.26. It is deduced that Eu^{3+} replace La1 with the symmetry of C_{2v} . So only one ${}^5D_0 \rightarrow {}^7F_0$ transition is observed.

As shown in Fig. 4 the excitation spectrum of NLBO:Tb^{3+} (10%) is a broad band in 230–300 nm range from the $4f^8 \rightarrow 4f^7 5d^1$ transition of Tb^{3+} and many weak peaks in 300–400 nm range from the $4f \rightarrow 4f$ transition of

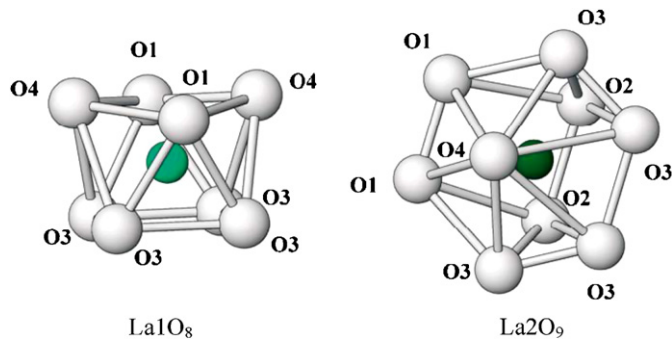


Fig. 3. Coordination polyhedra of the La1, La2 cations [14,20].

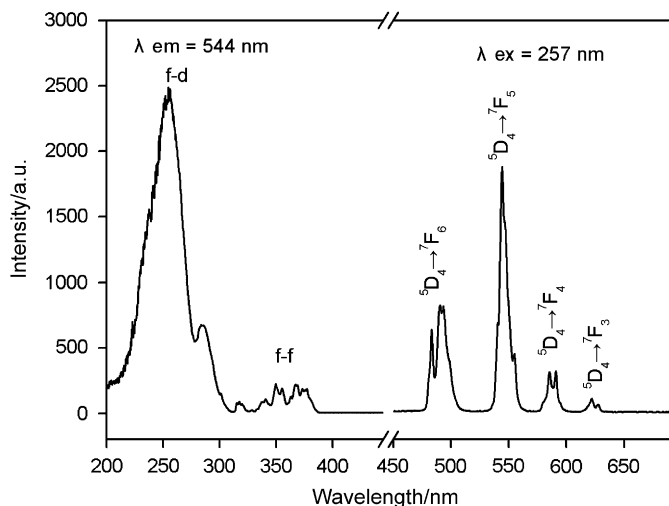


Fig. 4. Excitation and emission spectra of NLBO:Tb^{3+} (10%)

Tb^{3+} . This type of behavior is also observed in many Tb^{3+} -doped materials, for example $\text{CaYBO}_4:\text{Tb}$ [23], $\text{CaLaP}_3\text{O}_{10}:\text{Tb}$ [24] and $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Tb}$ [25]. Right part in Fig. 4 exhibits the emission spectrum of Tb^{3+} -doped NLBO excited at 257 nm. It consists of typical Tb^{3+} emission due to the ${}^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transition, which are ${}^5D_4 \rightarrow {}^7F_6$ (483, 490, 493 nm), ${}^5D_4 \rightarrow {}^7F_5$ (544, 555 nm), ${}^5D_4 \rightarrow {}^7F_4$ (585, 590 nm), ${}^5D_4 \rightarrow {}^7F_3$ (621, 627 nm), respectively. Among them the emission at 544 nm is the strongest.

We record the relative intensity of NLBO:Eu at 613 nm and NLBO:Tb at 544 nm as functions of doping concentrations. Concentration dependence of the emission intensity is shown in Fig. 5. Because of concentration quenching, the emission intensity increases, and then decreases. NLBO:Eu and NLBO:Tb exhibited weak concentration quenching and the quenching concentration is 30% for NLBO:Eu and 10% for NLBO:Tb . This is possibly attributed to the high degree of covalency of BO_3 anions and larger interatomic distance of rare-earth ions in $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8$ structure.

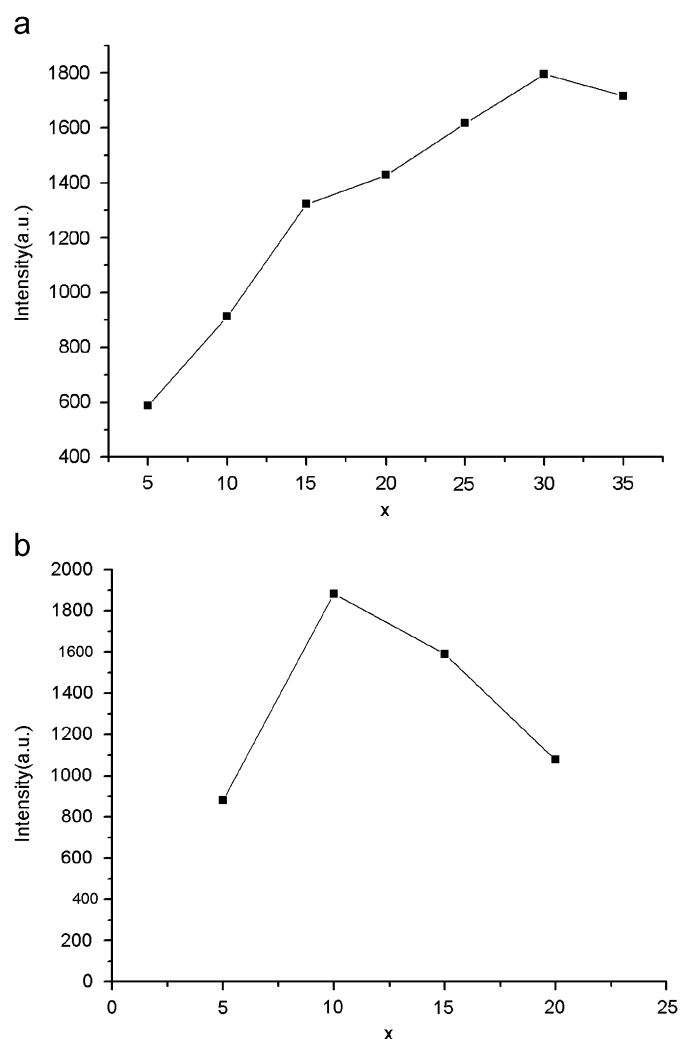


Fig. 5. Concentration dependence of the emission intensity of (a) NLBO:Eu (b) NLBO:Tb .

4. Conclusions

$\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{Eu}^{3+}$ (NLBO:Eu) and $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{Tb}^{3+}$ (NLBO:Tb) have been synthesized by solid-state reaction. PL spectra show that the dominated emission of NLBO:Eu located at 613 nm is from the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ and the emission at 589 and 598 nm originates from the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$. We can deduce that Eu^{3+} is located at the site of non-inversion symmetry and Eu^{3+} is substituted for La1 with the symmetry of C_{2v} . NLBO:Tb emit bright green luminescence centered at 544 nm attributed to the transition ${}^5D_4 \rightarrow {}^7F_5$. $\text{Na}_3\text{La}_9\text{O}_3(\text{BO}_3)_8:\text{RE}^{3+}$ ($\text{RE} = \text{Eu}, \text{Tb}$) may be a novel choice as phosphor material for lamps and display applications.

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